THE REACTION OF TRIPHENYLMETHYL WITH STYRENE AND OTHER POLYMERIZABLE VINYL DERIVATIVES

BY

JAMES OLIVER CORNER, JR.

A.B., Dartmouth College, 1939

M.A., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1942

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THE REACTION OF TRIPHENYLMETHYL WITH STYRENE AND OTHER POLYMERIZABLE VINYL DERIVATIVES

Introduction

Previous work in this Laboratory[1] has indicated that the free radical tribiphenylmethyl reacts with styrene to produce a compound composed of two free radical units and one styrene molecule. One of the objects of the present investigation was to prove the structure of this compound or of compounds very similar to it. Triphenylmethyl was used as the free radical in order to obtain a product which might be synthesized. Furthermore, the methods of synthesis attempted offered an opportunity to study some reactions of compounds containing the trityl group.

Discussion of Results

Triphenylmethyl was found to react with styrene, *p*-chlorostyrene and *m*-nitrostyrene to give products composed of two free radical units and one styrene molecule. Triphenylmethyl can add in the 1,4 position of diolefins containing a conjugated system of double bonds.[2] The free radical can also add across the double bond in maleic anhydride.[2] Thus there are two possible structures for the triphenylmethyl-styrene addition product corresponding to addition in the 1,2 or 1,4 position. Various degradation methods designed to differentiate between the two possibilities were unsuccessful. One scheme involved the attempted oxidation of the sensitized aromatic ring obtained by reduction of the triphenylmethyl-*m*-nitrostyrene addition product to the amino compound. The diacetamide of the amine was prepared.

The starting material for several attempted syntheses of the triphenylmethyl-styrene addition product was β,β,β-triphenylpropionic acid. An improved method for the preparation of this compound was developed.

1,1,1,4,4,4-Hexaphenylbutanone was prepared from β,β,β-triphenylpropionyl chloride and triphenylmethylsodium.[3] The

carbonyl and methylene groups in such a compound would be subject to a great deal of steric hindrance. This ketone proved to be very unreactive toward a variety of reagents.

2,2,2-Triphenylpropiophenone was prepared from β,β,β-triphenylpropionamide and phenylmagnesium bromide by the method of Suter and Weston.[4] The structure of the ketone was proved by (1) preparation of the oxime and (2) catalytic hydrogenation to the known hydrocarbon, 1,1,1,3-tetraphenylpropane.[3]

2,2,2-Triphenylpropiophenone was reduced to 1,3,3,3-tetraphenyl-1-propanol by means of aluminum isopropoxide. Dehydration of this alcohol yielded 1,1,1,3-tetraphenylpropene, probably the *trans* form. The olefin was identified by the fact that catalytic hydrogenation converted it to 1,1,1,3-tetraphenylpropane. An attempted side-chain bromination of the latter compound also produced 1,1,1,3-tetraphenylpropene.

The reaction of 1,2,2,2-tetraphenylethanol with thionyl chloride and pyridine or with phosphorus tribromide was found to produce only tetraphenylethylene indicating that a retropinacolone rearrangement[5] had occurred.

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VITA

The writer was born in Toronto, Ontario, Canada, July 19, 1917. He attended the public schools of Oklahoma, City, Okla., Yonkers, N. Y., Sioux City, Iowa, Canton, Ohio, and Mt. Lebanon, Pa. He graduated from Mt. Lebanon High School in January, 1935. In the fall of 1935 he entered Dartmouth College and received the Bachelor of Arts degree in June, 1939. In September of that year he entered the graduate School of the University of Illinois and received the degree of Master of Arts in June, 1940. He served as assistant in chemistry from September, 1940 to August, 1941. From September, 1941 to July, 1942, he held a Monsanto Fellowship.

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